PATENT SPECIFICATION (11) 1 547 280

1 547 280

(21) Application No. 31804/76 (22) Filed 30 July 1976
(31) Convention Application No. 2 534 188
(32) Filed 31 July 1975 in
(33) Fed. Rep. of Germany (DE)
(44) Complete Specification published 6 June 1979
(51) INT CL² B32B 17/04, 27/04, 27/06, 27/20
(52) Index at acceptance
B5N 1704 2704 2706 2720
B5A 1R151 1R158 1R214D 1R214F 1R314C1C 1R314C1D 1R314C1E 1R314C1F 1R314C1S 1R314C1X 1R314C6 1R322 1R420 1R422 T16F

(19)

(54) MOLDINGS WITH A SMOOTH SURFACE, MADE FROM GLASS FIBER-REINFORCED PLASTICS MATERIAL

(71) We, BASF AKTIENGESELLSCHAFT, a German Joint Stock Company of 6700 Ludwigshafen, Federal Republic of Germany, do hereby declare the invention, for which we pray that a patent may be granted to us and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to moldings with a smooth surface, made from glass fiber-reinforced plastics material.

Mechanically strong moldings of glass fiber-reinforced plastics material, which contain fibrous substances in which the fiber lengths are relatively large, namely 10 mm or more, may be manufactured by the process disclosed in German Laid-Open Application DOS 1,454,988. For example, in this process cut pieces of sheets of thermoplastics reinforced with glass fiber mats are heated outside the mold until the thermoplastics material exhibits plastic flow, and are then shaped in molds which are at a temperature below the softening point of the thermoplastics material. Even under optimum process conditions, the moldings thus obtained have a rough surface which shows fibers, and this greatly restricts the use of such materials.

There are various possible ways of improving the surface. If, in the manufacture of moldings of glass fiber-reinforced plastics, mats of A- or E-glass fibers of diameter from 6 to 15 μ are used, the weight per unit area of the mats being from 15 to 100 g/m², the surface roughness of the sheeting is substantially reduced. However, on deep-drawing or pressing the latter to give the final molding, the glass fiber mats tear, especially if they have to undergo substantial deformation. Even when manufacturing moldings which are only slightly curved, the surface quality of the sheeting is not retained. It is true that if polymer fibers, or mats of polymer fibers, are used to manufacture the moldings, the process gives moldings having smooth surfaces. However, the polymer fibers or fiber mats do not have the heat resistance required for processing, so that the mechanical properties of the moldings prove unsatisfactory. The surface of the moldings can also be improved by laminating films onto them. However, this process is worth carrying out only if, in addition, an intermediate layer of a surfacing mat which is as thick as possible and weighs at least 30 g/m² is introduced between the sheeting and the film. This intermediate layer is intended to prevent the glass fiber bundles of the glass fiber mats from pressing through the films during molding.

The present invention seeks to provide moldings with a smooth surface from a plastics material reinforced with long glass fibers.

According to the invention there is provided a molding with a smooth surface, comprising

(a) a stable base layer of a plastics material reinforced with glass fibers which are at least 10 mm long, in an amount of from 5 to 50% by volume, based on the base layer, and

(b) a surface layer firmly bonded to (a) at at least one of its surfaces, wherein the surface layer, or at least one of the surface layers, (b) is a film of a plastics material, from 50 to 1,000 μm thick, which is filled with from 3 to 40 per cent by volume, based on the total film material, of a solid filler which either has a non-fibrous structure with a particle size of from 5 to 200 μm, preferably from 5 to 50 μm, or has a fibrous structure with a diameter of from 6 to 15 μm and a fiber length of from 20 μm to 1 mm.

The plastics material of the surface layer(s) (b) can have a higher molecular weight than the glass fiber-reinforced plastics material (a), and the plastics material in the surface layer(s) (b) need not be identical with the glass fiber-reinforced plastics material (a) but can be instead weldable thereto.

Preferred fillers are glass beads, short glass fibers, inorganic minerals or metal powders.

Moldings are to be understood as articles made by shaping thermoplastics molding compositions in molds, without machining. Above all, they are produced by molding under pressure. The surface quality of pressed moldings depends substantially on the surface quality of the wall of the press mold. On pressing the glass fiber-reinforced plastics material, the surface quality is above all impaired by the glass fiber bundles which are pressed into the surface during pressing. For the purposes of the invention, a molding of glass fiber-reinforced plastics material is considered to have a smooth surface if the surface has substantially the smoothness that would be obtained on pressing the same plastics material not reinforced with glass fibers, that is to say a flawless surface free from glass fibers which have been forced out, and indeed free from visible glass fibers. The stable base layer of the moldings according to the invention is the glass fiber-reinforced plastics material. The glass fibers used as reinforcement in the base layer are those having a length of 10 mm or more. For reinforcing the plastics material, the glass fibers may be employed as individual fibers or, preferably, as glass fiber mats. Preferred plastics materials are those which have a G-modulus, measured according to DIN 53,445, of at least 1,000. Such plastics are, in particular, vinyl polymers, e.g. polystyrene, copolymers of styrene with other comonomers, especially with acrylonitrile, high pressure polyethylene, low pressure polyethylene, polypropylene, copolymers of ethylene and propylene, polyvinyl chloride and vinyl chloride copolymers, polymers of acrylic acid esters and methacrylic acid esters, polyamides, e.g. polycaprolactam and polycarbonates. The content of glass fibers, e.g. as mat, in the base layer, based on the total mixture in that layer, is from 5 to 50 per cent by volume, preferably from 10 to 30 per cent by volume. The manufacture of the plastics material reinforced with glass fiber mats is described in German Laid-Open Applications DOS 1,454,988 and 2,312,816.

The surface layer(s) firmly bonded to the surface of the glass fiber-reinforced plastics are films which are compatible with the base layer, i.e. which will weld to the base layer during manufacture of the sheeting. The surface layer, i.e. the film, must not detach during use of the molding, even under extreme conditions, e.g. severe temperature fluctuation. The most advantageous conditions prevail if the plastics material of the surface film(s) consists of the same material as the plastics material of the base layer. However, the plastics material of the surface layer(s) need not be identical with the glass fiber-reinforced plastic(s) material. In fact, we have found that it can be of advantage, as regards surface quality, if the plastics material of the covering film(s) has a higher molecular weight than the glass fiber-reinforced plastics material. The surface film is prefabricated in a thickness of from 50 to 1,000 μm, preferably from 200 to 600 μm, and is then laminated onto the base during manufacture of the reinforced sheeting, e.g. by the process of German Laid-Open Application DOS 2,312,816, by simply feeding the film onto one or both sides of the base layer. Preheating of the film facilitates welding onto the base layer.

Any thermoplastically processable plastics material may be used for the surface layer. In particular, olefin polymers, polyamides, styrene polymers, polyesters, vinyl chloride polymers and mixtures of these polymers may be used. Specific examples are high pressure polyethylene and low pressure polyethylene, ethylene-propylene copolymers, polypropylenes, especially those of which the structure shows a high degree of steric regularity, styrene homopolymers and copolymers, especially styrene-acrylonitrile copolymers and rubber-modified styrene homopolymers and copolymers, polyvinyl chloride, nylon-6, nylon-12 and nylon-6,6, polyester resins based on terephthalic acid, polyphenylene oxides and polyoxymethylenes.

The filler present in the surface layer(s) has a particle size (mean diameter) of from 5 to 200 μm, where non-fibrous, e.g. spherical, granular or flake-like, solid fillers are concerned. If the solid filler is fibrous, it will have a diameter of from 6 to 15 μm and a fiber length of from 20 μm to 1 mm. The surface layer(s) contain from 3 to 40 per cent by volume of filler, based on the total film material. A preferred filler concentration is from 5 to 20 per cent by volume.

Particularly suitable fillers are glass beads of diameters from 5 to 200 μm and short glass fibers with diameters of from 6 to 15 μm and lengths from 20 μm to 1 mm, such as are used in mixtures for injection molding. However, granular and flake-like, organic or inorganic fillers may also be employed. For example, special effects are achievable with films filled with metal powders. Examples of suitable inorganic fillers are chalk, talc, kaolin, calcined kaolin and calcium silicate, e.g. wollastonite. The particle size should preferably not exceed 50 μm and particularly not exceed 20 μm. In addition to the filler(s) the surface layer(s) may also contain a transparent or opaque organic pigment which makes subsequent surface-coating superfluous. Such laminated sheeting has a smooth, flawless surface after shaping. The moldings may be used, without further after-treatment, for applications where their visual appearance matters.

Example 1.

Using an extruder and a sheet die, a polypropylene film filled with 10% by volume of

glass beads of mean particle size 25 μm and 2% by volume of a pigment of mean particle size about 1 μm is produced and is calibrated to a thickness of 500 μm in a downstream calender. A sheeting is manufactured from a polypropylene melt and 2 glass mats each weighing 600 g/m² on an apparatus as shown in Figure 1 of German Laid-Open Application DOS 2,312,816, and at the same time one of the above filled surface films is fed onto each side of the article being produced, the films being heated by infra-red radiators, on the sides facing the mats, to the melting point of polypropylene. The sheet-like article thus produced is then punched to size, heated to about 230°C in an infra-red oven and pressed in a cold metal mold. The pressing can be removed from the mold after a cooling time of 20 seconds. The surface quality is comparable with that of normal non-reinforced injection moldings and the glass fibers of the mats have not been pressed through.

Example 2.

A film 800 μm thick is produced from a polyethylene which has a density of 0.96 g/cm³ and a melt index of 0.5 g/10 minutes (190°C, 2.16 kg — ASTM-D 1238-65 T) and which is filled with 15% by volume of short glass fibers having a mean length of 0.4 mm and a thickness of 10 μm. The base layer is formed from a polyethylene which has a density of 0.96 g/cm³ and a melt index of 5 g/10 minutes, and from 2 glass mats each weighing 600 g/m², and a film of the above type is laminated onto each side of the base layer. For comparison, two non-reinforced films of the same thickness are laminated onto the sheeting under the same conditions. In both cases, the product exhibits the same surface quality.

To manufacture a dish, the sheeting is punched to size, heated at 210°C in an oven with air circulation and then pressed in a cold metal mold. In the case of the article with the non-reinforced surface film, the glass fibers of the mat reinforcement can be seen and felt on the surface, whilst the article with the reinforced surface film is completely smooth.

Example 3.

A sheeting is produced from polystyrene and 2 glass fiber mats weighing 450 g/m², and its surfaces are covered with two 400 μm thick films of a styrene-acrylonitrile copolymer containing 8% by volume of glass beads of mean particle size 25 μm and 2% by volume of titanium dioxide of mean particle size about 1 μm.

Strips of this sheeting are heated to about 240°C between infra-red radiators and are pressed in a steel mold to form mudguards. The articles have a white, glossy, smooth surface which requires no subsequent surface-coating.

WHAT WE CLAIM IS:—

1. A molding with a smooth surface, comprising (a) a stable base layer of a plastics material reinforced with from 5 to 50% by volume, based on the base layer, of glass fibers which are at least 10 mm long, and (b) a surface layer firmly bonded to (a) at at least one of its surfaces, wherein the, or at least one of the surface layers (b) is a film of a plastics material, from 50 to 1,000 μm thick, which is filled with from 3 to 40 per cent by volume, based on the total film material, of a solid filler which either has a non-fibrous structure with a particle size of from 5 to 200 μm or has a fibrous structure with a diameter of from 6 to 15 μm and a fiber length of from 20 μm to 1 mm.

2. A molding as claimed in claim 1, wherein the plastics material of the surface layer(s) (b) has a higher molecular weight than the glass fiber-reinforced plastics material (a).

3. A molding as claimed in claim 1 or 2, wherein the plastics material of the surface layer(s) (b) is not identical with the glass fiber-reinforced plastics material (a) but is weldable thereto.

4. A molding as claimed in any of claims 1 to 3, wherein the filler in (b) is glass beads, short glass fibers, an inorganic mineral or a metal powder.

5. A molding as claimed in claim 1, 2 or 4, wherein the plastics material of the base layer and the plastics material of the surface layer(s) are identical and are polyethylene, polypropylene, an ethylene-propylene copolymer, polystyrene, a styrene copolymer or polyvinyl chloride.

6. A molding with a smooth surface substantially as described in any of the foregoing Examples.

J. Y. & G. W. JOHNSON,
Furnival House,
14—18 High Holborn,
London WC1V 6DE,
Chartered Patent Agents,
Agents for the Applicants.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1979.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.